

data sheet. If noticeable leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Sample Preparation. Treat the contents of each sample container as described below:

11.2.1 Container No. 1 (Probe, Filter, and Impinger Catches). Filter this container's contents, including the sampling filter, through Whatman No. 541 filter paper, or equivalent, into a 1500-ml beaker.

11.2.1.1 If the filtrate volume exceeds 900 ml, make the filtrate basic (red to phenolphthalein) with NaOH, and evaporate to less than 900 ml.

11.2.1.2 Place the filtered material (including sampling filter) in a nickel crucible, add a few ml of water, and macerate the filters with a glass rod.

11.2.1.2.1 Add 100 mg CaO to the crucible, and mix the contents thoroughly to form a slurry. Add two drops of phenolphthalein indicator. Place the crucible in a hood under infrared lamps or on a hot plate at low heat. Evaporate the water completely. During the evaporation of the water, keep the slurry basic (red to phenolphthalein) to avoid loss of  $F^-$ . If the indicator turns colorless (acidic) during the evaporation, add CaO until the color turns red again.

11.2.1.2.2 After evaporation of the water, place the crucible on a hot plate under a hood, and slowly increase the temperature until the Whatman No. 541 and sampling filters char. It may take several hours to char the filters completely.

11.2.1.2.3 Place the crucible in a cold muffle furnace. Gradually (to prevent smoking) increase the temperature to 600 °C (1100 °F), and maintain this temperature until the contents are reduced to an ash. Remove the crucible from the furnace, and allow to cool.

11.2.1.2.4 Add approximately 4 g of crushed NaOH to the crucible, and mix. Return the crucible to the muffle furnace, and fuse the sample for 10 minutes at 600 °C.

11.2.1.2.5 Remove the sample from the furnace, and cool to ambient temperature. Using several rinsings of warm water, transfer the contents of the crucible to the beaker containing the filtrate. To ensure complete sample removal, rinse finally with two 20-ml portions of 25 percent  $H_2SO_4$ , and carefully add to the beaker. Mix well, and transfer to a 1-liter volumetric flask. Dilute to volume with water, and mix thoroughly. Allow any undissolved solids to settle.

11.2.2 Container No. 2 (Sample Blank). Treat in the same manner as described in Section 11.2.1 above.

11.2.3 Adjustment of Acid/Water Ratio in Distillation Flask. Place 400 ml of water in the distillation flask, and add 200 ml of concentrated  $H_2SO_4$ . Add some soft glass beads and several small pieces of broken glass tubing, and assemble the apparatus as shown in

Figure 13A-2. Heat the flask until it reaches a temperature of 175 °C (347 °F) to adjust the acid/water ratio for subsequent distillations. Discard the distillate.

CAUTION: Use a protective shield when carrying out this procedure. Observe standard precautions when mixing  $H_2SO_4$  with water. Slowly add the acid to the flask with constant swirling.

11.3 Distillation.

11.3.1 Cool the contents of the distillation flask to below 80 °C (180 °F). Pipet an aliquot of sample containing less than 10.0 mg  $F^-$  directly into the distillation flask, and add water to make a total volume of 220 ml added to the distillation flask. (To estimate the appropriate aliquot size, select an aliquot of the solution, and treat as described in Section 11.4.1. This will be an approximation of the  $F^-$  content because of possible interfering ions.)

NOTE: If the sample contains chloride, add 5 mg of  $Ag_2SO_4$  to the flask for every mg of chloride.

11.3.2 Place a 250-ml volumetric flask at the condenser exit. Heat the flask as rapidly as possible with a Bunsen burner, and collect all the distillate up to 175 °C (347 °F). During heatup, play the burner flame up and down the side of the flask to prevent bumping. Conduct the distillation as rapidly as possible (15 minutes or less). Slow distillations have been found to produce low  $F^-$  recoveries. Be careful not to exceed 175 °C (347 °F) to avoid causing  $H_2SO_4$  to distill over. If  $F^-$  distillation in the mg range is to be followed by a distillation in the fractional mg range, add 220 ml of water and distill it over as in the acid adjustment step to remove residual  $F^-$  from the distillation system.

11.3.3 The acid in the distillation flask may be used until there is carry-over of interferences or poor  $F^-$  recovery. Check for interference and for recovery efficiency every tenth distillation using a water blank and a standard solution. Change the acid whenever the  $F^-$  recovery is less than 90 percent or the blank value exceeds 0.1 µg/ml.

11.4 Sample Analysis.

11.4.1 Containers No. 1 and No. 2.

11.4.1.1 After distilling suitable aliquots from Containers No. 1 and No. 2 according to Section 11.3, dilute the distillate in the volumetric flasks to exactly 250 ml with water, and mix thoroughly. Pipet a suitable aliquot of each sample distillate (containing 10 to 40 µg  $F^-$ /ml) into a beaker, and dilute to 50 ml with water. Use the same aliquot size for the blank. Add 10 ml of SPADNS mixed reagent (Section 7.3.13), and mix thoroughly.

11.4.1.2 After mixing, place the sample in a constant-temperature bath containing the standard solutions for 30 minutes before reading the absorbance on the spectrophotometer.